1,7-Dimethylchrysene. Photocyclisation of 1,6-Diarylhexa-1,3,5-trienes

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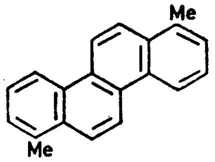
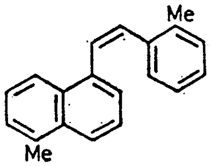
1,7-Dimethylchrysene has been synthesised from 1,5-diacetylnaphthalene and by photocyclisation of 1,6-di-(*o*-tolyl)hexa-1,3,5-triene. Irradiation of 1-(2-naphthyl)-6-phenylhexa-1,3,5-triene did not lead to the expected benzo[*c*]chrysene or naphth[2,1-*a*]anthracene.

ONE of us has previously[1] described a synthesis of 1,7-dimethylchrysene (I) by photocyclisation of 1-methyl-5-(*o*-methyl-α-styryl)naphthalene (II). The highly crystalline hydrocarbon had m.p. 298—299 °C and its physical properties were in accord with the proposed structure. More recently,[2] Mukherji, Dabas, and Sharma, without reference to the earlier work, have reported the synthesis of another hydrocarbon, m.p. 129 °C, which they regard as 1,7-dimethylchrysene. To resolve the discrepancy we have synthesised 1,7-dimethylchrysene by an unequivocal route and this establishes the correctness of the original work.

The starting material was 1,5-diacetylnaphthalene, prepared by acetylation of naphthalene as described by Stephan.[3] The orientation of the acetyl groups in this compound was confirmed by oxidation with hypochlorite to naphthalene-1,5-dicarboxylic acid identified by comparison of the dimethyl ester with an authentic specimen. The derived dibromide[4] (III; R = Br) was converted into naphthalene-1,5-dicarbonyldipropionic acid (III; $R = CH_2{\cdot}CO_2H$) by reaction with diethyl sodiomalonate in benzene followed by hydrolysis and decarboxylation of the product with hydrochloric acid, and thence by Huang-Minlon reduction into the corresponding dibutyric acid. The latter was smoothly cyclised with polyphosphoric acid to give the diketone (IV), the structure of which was confirmed by its conversion into chrysene by reduction with lithium aluminium hydride and dehydration–dehydrogenation of the product by heating with palladium. In line with the proposed structure the u.v. spectrum of the diketone (IV) resembled that of 3,4-dihydrophenanthrene-1(2*H*)-one and other 2-acylnaphthalenes in showing three regions of absorption between 220 and 380 nm.[5] Reaction of the diketone (IV) with methylmagnesium iodide and dehydration–dehydrogenation of the product with palladium afforded 1,7-dimethylchrysene, m.p. 296—297 °C, identical with the product obtained previously.[1]



(I)



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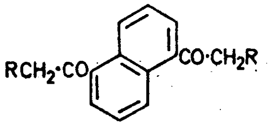

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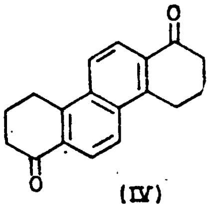

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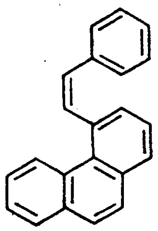

(V)

A similar sequence of reactions with the product from reaction of the dibromide (III; R = Br) with diethyl

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[3] R. Stephan, *Chem. Ber.*, 1957, **90**, 296.

[4] F. Mayer, *Annalen*, 1931, **488**, 259.

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sodiomethylmalonate afforded 1,2,7,8-tetramethylchrysene, apparently identical with the product previously obtained[6] by a route which involved a dehydrogenative cyclisation with aluminium chloride, a procedure which may bring about loss or migration of alkyl substituents.[7]

Photocyclisation of stilbene analogues[8] and of 1,4-diarylbutadienes[9] is now a well established route to a variety of polycyclic aromatic hydrocarbons and heterocyclic compounds. The conversion of 1,6-diphenylhexa-1,3,5-triene into chrysene has been reported by Fonken[10] and recently Leznoff and Hayward[11] have reported the synthesis of a number of chrysene derivatives from substituted diphenylhexatrienes, and of picene from 1-(1-naphthyl)-6-phenylhexa-1,3,5-triene. We have been working with closely related compounds and we report here some results additional to those recorded by Leznoff and Hayward.

We have confirmed the formation of chrysene by irradiation of 1,6-diphenylhexa-1,3,5-triene, but we found that the success of the reaction was dependent on the experimental conditions, a point not sufficiently emphasised in the original publication. For example, irradiation of an ethereal solution of the hexatriene (3×10^{-3} mol dm^{-3}) through quartz with light from a medium-pressure mercury lamp in the presence of iodine or atmospheric oxygen as oxidant gave an amorphous product showing only weak absorption above 240 nm; no chrysene was detected. With a more dilute solution (7×10^{-4} mol dm^{-3}) in benzene, however, and light from a medium- or, better, a high-pressure mercury lamp, chrysene was obtained in 12% yield, comparable to that originally claimed. Under the same conditions 1,6-di-(*o*-tolyl)hexa-1,3,5-triene gave 1,7-dimethylchrysene, identical with the product obtained as already described, in 7% yield. Although the yields in the final step are modest, the directness of this approach to chrysene derivatives offers some advantages over more lengthy published procedures. Nothing is yet known of the mechanism of these reactions, but it seems reasonable to suppose that they proceed in a stepwise manner leading first to the 1-(α-styryl)naphthalene derivative [as (II)], which subsequently cyclises to the chrysene. The ready photocyclisation of 1-(α-styryl)naphthalenes to chrysenes has been recorded.[1,12]

We have also studied the photocyclisation of 1-(2-naphthyl)-6-phenylhexa-1,3,5-triene which we hoped might afford a convenient route to naphth[2,1-*a*]anthracene or, more probably, benzo[*c*]chrysene. In fact under a wide variety of conditions only ill defined amorphous products have been obtained from this reaction; neither of the desired polycyclic hydrocarbons has been detected (see Experimental section). Whether this failure is due to electronic (*cf*. ref. 13) or steric effects is at present uncertain. Initial reaction would be expected to take place at the α-position of the naphthalene nucleus[14] leading to 4-(α-styryl)phenanthrene (V) by way of a dihydro-derivative, but it may well be that this step is sufficiently slowed down by steric factors to allow alternative reactions to supervene. The ready photocyclisation of 4-(α-styryl)phenanthrene to benzo[*c*]chrysene has already been reported.[15]

The 1,6-di-(*o*-tolyl)hexa-1,3,5-triene used in our experiments was readily obtained from *o*-methylcinnamyltriphenylphosphonium periodate by action of lithium ethoxide.[16] Alternative procedures[17] for effecting this 'dimerisation' by reaction of the corresponding phosphonium bromide with oxygen or sulphur failed in our hands. The hexatriene was obtained as a single crystalline isomer which we believe is the all-*trans* compound; the u.v. spectrum showed no '*cis*' peak in the region 250—270 nm (*cf*. ref. 18) and the i.r. spectrum was similar to that of all-*trans*-1,6-diphenylhexa-1,3,5-triene[19] except for the presence of weak absorption at 788 cm^{-1}.

1-(2-Naphthyl)-6-phenylhexa-1,3,5-triene was prepared from 3-(2-naphthyl)acrylic acid. Reduction of the methyl ester with lithium aluminium hydride and aluminium chloride[20] gave the corresponding allyl alcohol, which was converted into the bromide and thence into the triphenylphosphonium bromide. Reaction of the latter with ethanolic lithium ethoxide in presence of cinnamaldehyde gave the hexatriene as a mixture of the all-*trans*- and the *trans,cis,trans*-forms, which were readily separated by chromatography on alumina.

EXPERIMENTAL

U.v. spectra, measured with a Unicam SP 800 spectrometer, refer to solutions in 95% ethanol unless otherwise stated. Routine i.r. spectra were measured with a Perkin-Elmer Infracord, and high resolution spectra with a Hilger–Watts H 900 double-beam spectrometer. Mass spectra were recorded with a Hitachi RMU 60 instrument

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and ^1H n.m.r. spectra with a Perkin-Elmer 60 MHz instrument for solutions in carbon tetrachloride or deuteriochloroform, with tetramethylsilane as internal reference. Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise stated.

Naphthalene-1,5-*dicarbonyldipropionic Acid* (III; R = $CH_2{\cdot}CO_2H$).—A solution of 1,5-bis-2-bromoacetylnaphthalene [4] (20 g) in benzene (2 l) was added to a suspension of diethyl sodiomalonate [from sodium hydride (2·8 g) and diethyl malonate (18·5 g)] in benzene (150 ml), and the mixture was boiled for 24 h. The cooled solution was washed with water and dried, and benzene and excess of diethyl malonate were removed under reduced pressure. The residual oil was boiled with a mixture of acetic acid (600 ml), water (300 ml), and hydrochloric acid (425 ml) for 42 h; the solution was concentrated to remove most of the acetic acid and diluted with water, and the precipitate (19 g) was filtered off. Crystallisation from acetic acid or benzene–acetone afforded the *diacid* as prisms (9 g), m.p. 199—200 °C (decomp.) (Found: C, 65·7; H, 5·0%; M^+, 328. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%; *M*, 328). The *dimethyl ester*, prepared with diazomethane, formed needles in benzene, m.p. 100—101 °C (Found: C, 67·6; H, 5·7. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%).

Naphthalene-1,5-*dibutyric Acid*.—The foregoing acid (10 g) was reduced by the Huang-Minlon procedure with sodium hydroxide (12 g), and hydrazine hydrate (99%; 13 ml) in diethylene glycol (250 ml). The *dibutyric acid* (7 g) was obtained as crystals from acetic acid, m.p. 228—230 °C (Found: C, 71·42; H, 6·5. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7%). The *dimethyl ester*, prepared with diazomethane, formed needles in methanol, m.p. 68 °C (Found: C, 73·4; H, 7·5. $C_{20}H_{24}O_4$ requires C, 73·1; H, 7·4%).

2,3,4,8,9,10-*Hexahydrochrysene*-1,7-*dione* (IV).—A mixture of the foregoing dibutyric acid (250 mg) and polyphosphoric acid (10 ml) was warmed at 80—90 °C for 5 h with occasional stirring, cooled, and poured into water; the precipitate was washed with sodium carbonate solution and chromatographed on alumina. Elution with benzene afforded the *diketone* (102 mg) as blades, m.p. 291—292° C (from benzene) (Found: C, 81·9; H, 6·1%; M^+, 264. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%; *M*, 264); $\lambda_{max.}$ 237, 252sh, 259, 281, 292, 302, 360, and 379 nm (log ε 3·90, 4·19, 4·43, 3·57, 3·75, 3·78, 3·01, and 3·07).

The ketone (50 mg) was reduced with lithium aluminium hydride (500 mg) in refluxing ether–benzene (1 : 1; 20 ml) for 3 h. The crude product (48 mg) was heated with 10% palladised charcoal (100 mg) at 250 °C for 30 min, gradually rising to 300 °C over a further 30 min. The crude product was extracted with benzene; crystallisation from benzene–ethanol afforded chrysene as plates (28 mg), m.p. and mixed m.p. 252—254 °C.

1,7-*Dimethylchrysene* (I).—A solution of the preceding dione (100 mg) in benzene (10 ml) was added to a solution of methylmagnesium iodide [from magnesium (40 mg) and methyl iodide (0·4 ml)] in ether (10 ml), and the mixture was boiled for 5 h. The crude product was dehydrated by refluxing with a crystal of iodine in xylene solution. Difficulty was experienced in taking the Grignard reaction to completion, and the reaction with methylmagnesium iodide was repeated with the dehydrated product until the crude product no longer showed i.r. carbonyl absorption. The total crude product was heated with 10% palladised charcoal (100 mg) at 275—300 °C for 1 h. Chromatography of the product on alumina and elution with benzene then afforded 1,7-dimethylchrysene (64 mg) as plates, m.p. and mixed m.p.[1] 296—297 °C (from benzene) (Found: C, 93·4; H, 6·6. Calc. for $C_{20}H_{16}$: C, 93·7; H, 6·3%); $\lambda_{max.}$ 226, 230, 243sh, 254sh, 262, 271, 288, 301, 313, 328, 348, 352, and 366 nm (log ε 4·24, 4·28, 3·97, 4·33, 4·58, 4·81, 3·74, 3·79, 3·93, 3·93, 2·92, 2·57, and 2·76). The 2,4,7-trinitrofluorenone complex formed orange-red needles in xylene, m.p. and mixed m.p. 254 °C.

Dimethyl Naphthalene-1,5-*bis*-(2-*methylbutyrate*).—Reaction of 1,5-bis-2-bromoacetylnaphthalene (20·2 g), diethyl methylmalonate (21 g), and sodium hydride (2·7 g) in benzene as described for compound (III; R = $CH_2{\cdot}CO_2H$) gave *naphthalene*-1,5-*dicarbonylbis*-(2-*methylpropionic acid*) (III; R = $CHMe{\cdot}CO_2H$) as prisms in benzene–methanol, m.p. 195—197° (Found: C, 67·7; H, 6·0. $C_{20}H_{20}O_6$ requires C, 67·4; H, 5·7%). This acid (4 g) was reduced as described for naphthalene-1,5-dibutyric acid. It was found easiest to purify the crude product (3·2 g) as the dimethyl ester, prepared with diazomethane in ether–methanol. Chromatography on acid-washed alumina and elution with benzene–light petroleum (2 : 3) gave the *dibutyrate* (1·2 g) as blades, m.p. 83° (from light petroleum) (Found: C, 74·0; H, 7·7%; M^+, 356. $C_{22}H_{28}O_4$ requires C, 74·1; H, 7·9%; *M*, 356).

2,3,4,8,9,10-*Hexahydro*-2,8-*dimethylchrysene*-1,7-*dione*.—A mixture of the foregoing diester (300 mg) and polyphosphoric acid (30 ml) was heated at 90—95 °C for 5 h with occasional mixing, cooled, and poured into water; the precipitate was filtered off and digested with sodium hydroxide solution. The neutral material was chromatographed on alumina. Elution with benzene–light petroleum (3 : 1) removed a small amount of impurity and then afforded the *diketone* (190 mg) as plates, m.p. 242° (Found: C, 82·2; H, 6·6%; M^+, 292. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9%; *M*, 292). The u.v. spectrum was similar to that of the parent diketone, $\lambda_{max.}$ 238, 252, 260, 281, 292, 302, 344sh, 359, and 375 nm (log ε 4·46, 4·79, 4·99, 4·14, 4·29, 4·31, 3·39, 3·59, and 3·61).

1,2,7,8-*Tetramethylchrysene*.—This hydrocarbon was obtained from the foregoing dione and methylmagnesium iodide as described for the preparation of 1,7-dimethylchrysene. After chromatography on alumina it was obtained from benzene as plates, m.p. 303—304 °C (lit.,[6] 298—299 °C) (Found: C, 92·9; H, 7·1%; M^+, 284. Calc. for $C_{22}H_{20}$: C, 92·9; H, 7·1%; *M*, 284); $\lambda_{max.}$ 228, 238, 246, 257sh, 265, 275, 291sh, 303, 315, 329, 350, 354sh, and 370 nm (log ε 4·50, 4·53, 4·33, 4·57, 4·90, 5·14, 4·09, 4·08, 4·12, 4·11, 3·24, 2·64, and 3·05). The 2,4,7-*trinitrofluorenone complex* formed orange-red needles in benzene, m.p. 291—292 °C (Found: C, 70·7; H, 4·6; N, 6·8. $C_{35}H_{25}N_3O_7$ requires C, 70·1; H, 4·2; N, 7·0%).

1,6-*Di*-(o-*tolyl*)*hexa*-1,3,5-*triene*.—A solution of lithium ethoxide in ethanol (0·5 mol dm^{-3}; 35 ml) was added dropwise to a refluxing solution of *o*-methylcinnamyltriphenylphosphonium periodate (8·2 g) (prepared [16] from *o*-methyltriphenylphosphonium bromide) in ethanol (350 ml). A transient orange colour was observed and the mixture rapidly turned dark brown. Refluxing was continued for 2 h, solvent was evaporated off, and the resulting solid product (15·3 g) was adsorbed on silica gel which was added to the top of a column containing silica gel (700 g). Elution with benzene–light petroleum (1 : 4) afforded first a yellow oil (470 mg), which was not further examined, then a mixture of products, and finally the *hexatriene* (790 mg) as pale yellow flakes (from benzene), m.p. 132—133 °C

(Found: C, 92·4; H, 7·6%; M^+, 260. $C_{20}H_{20}$ requires C, 92·3; H, 4·7%; M, 260); $\lambda_{max.}$ (cyclohexane) 241, 346, 357, and 376 nm (log ε 3·92, 4·70, 4·70, and 4·47); $\nu_{max.}$ (KBr) 1601m (C=C), 1008s (*trans*-CH=CH), 753, and 718s (aromatic C–H) cm^{-1}.

3-β-*Naphthylallyl Alcohol.*—Methyl 3-β-naphthylacrylate (15 g) was reduced with lithium aluminium hydride (3·05 g) and aluminium chloride (3·5 g) in ether (450 ml) at room temperature for 0·5 h. The alcohol crystallised from benzene–light petroleum as plates (9·0 g), m.p. 115—116 °C (lit.,[21] 116 °C) (Found: C, 84·45; H, 6·4. Calc. for $C_{13}H_{12}O$: C, 84·75; H, 6·6%), $\nu_{max.}$ (Nujol) 3290s (OH), 1596m (C=C), 964, and 975s (*trans*-CH=CH) cm^{-1}.

3-β-*Naphthylallyl Bromide.*—A solution of 3-β-naphthylallyl alcohol (5·1 g) and phosphorus tribromide (5 g) in benzene (225 ml) was refluxed for 1 h. The washed (H_2O, Na_2CO_3) and dried solution was evaporated and the recovered bromide crystallised from benzene (m.p. 102 °C). It decomposed at room temperature and we were therefore unable to obtain a satisfactory elemental analysis; $\nu_{max.}$ (Nujol) 1584w (C=C) and 962s (*trans*-CH=CH) cm^{-1}; τ ($CDCl_3$) 5·8 (2H, d, CH_2Br), 3·3 (2H, m, olefinic), and 2·4 (7H, m, aromatic).

1-(2-*Naphthyl*)-6-*phenylhexa*-1,3,5-*triene*.—To a stirred solution of 3-(2-naphthyl)allyltriphenylphosphonium bromide (8·8 g; prepared from the foregoing naphthylallyl bromide and triphenylphosphine in boiling benzene) and cinnamaldehyde (2·5 g) in ethanol (110 ml) was added dropwise a solution of lithium ethoxide (92 ml; 0·2 mol dm^{-3}) at room temperature. The mixture was stirred at 35—40 °C for 3·5 h, cooled, and diluted with water (160 ml), and the yellow crystals (3·9 g) were collected and washed with 2 : 3 water–ethanol. Fractional crystallisation from benzene–light petroleum gave, as the less soluble isomer, *all*-trans-1-(2-*naphthyl*)-6-*phenylhexa*-1,3,5-*triene* as yellow flakes, m.p. 215—216 °C (Found: C, 93·4; H, 6·4%; M^+, 282. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%; M, 282); $\lambda_{max.}$ (cyclohexane) 216, 220, 245, 252, 260, 277, 290, 299, 306, 330, 347, 363, and 385 nm (log ε 4·49, 4·57, 4·01, 4·08, 3·99, 3·85, 4·10, 4·20, 4·14, 4·39, 4·71, 4·81, and 4·74). The mother liquors afforded the trans,cis,trans-*isomer* as yellow blades, m.p. 152 °C (Found: C, 93·6; H, 6·2%; M^+, 282); $\lambda_{max.}$ (cyclohexane) 216, 220, 255, 277, 290, 300, 306, 330, 346, 363, and 384 nm (log ε 4·60, 4·69, 4·31, 4·10, 4·24, 4·31, 4·27, 4·62, 4·84, 4·96, and 4·84).

Irradiation Experiments.—The light source was a Phillips HPK BA15D Type 57203B/00 high-pressure mercury vapour lamp, mounted externally to the reaction solution contained in a Pyrex vessel. The stirred solution of the diarylhexatriene (7·0 × 10^{-4} mol dm^{-3}) and iodine (3·6 × 10^{-3} mol dm^{-3}) in dry benzene was irradiated in air until the characteristic absorption of the triene had disappeared. The temperature of the solution was maintained at 30—35 °C by a cold finger immersed in the liquid. The solution was washed with sodium hydroxide solution and saturated brine, dried, and evaporated, and the products were examined by thin and preparative layer chromatography.

Irradiation of 1,6-di-(*o*-tolyl)hexa-1,3,5-triene in benzene for 24 h under these conditions gave 1,7-dimethylchrysene, in 7·2% yield after preparative layer chromatography and crystallisation from benzene–light petroleum, as plates, m.p. and mixed m.p. 297—298°; the 2,4,7-trinitrofluorenone complex formed orange-red needles in benzene, m.p. and mixed m.p. 256—257 °C.

Irradiation of 1-(2-naphthyl)-6-phenylhexa-1,3,5-triene (7·0 × 10^{-4} or 7·0 × 10^{-5} mol dm^{-3}) in benzene in the presence of iodine (3·6 × 10^{-4} mol dm^{-3}) gave a crude product which apparently (u.v. spectrum and t.l.c.) contained no benzo[*c*]chrysene or naphth[2,1-*a*]anthracene. Preparative layer chromatography of the crude amorphous product gave two fractions. The major fraction was a dark yellow powder, m.p. 95 °C, which appeared to contain iodine, and decomposed above its m.p. with evolution of purple fumes; it showed only three i.r. peaks (2990w, 2830w, and 1071s cm^{-1}) and three broad u.v. bands [$\lambda_{max.}$ (MeOH) 220, 291, and 337 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 25·6, 8·2, and 6·8)]. A second, very minor, product was a yellow solid, m.p. 45—50 °C (*m*/*e* 156). It showed aromatic u.v. absorption but we have not identified the chromophore: $\lambda_{max.}$ (cyclohexane) 239, 247, 260, 271, 280·5, 287·5, 291, 303, 312, 327, and 343 nm (log ε 4·52, 4·68, 3·62, 3·76, 3·87, 3·75, 3·79, 3·27, 2·94, 3·10, and 3·16).

When the irradiation was repeated in absence of iodine for periods of up to 60 h small amounts of the solid of m.p. 45—50 °C were again produced, but the main product was a yellow amorphous powder which showed no strong absorption above 250 nm.

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